

Carbon Nanotubes/Nanofibers by Plasma Enhanced Chemical Vapour Deposition

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Plasma enhanced chemical vapour deposition (PECVD) has been recently used for the production of vertically aligned carbon nanotubes/fibers (CN) directly on substrates. These structures are potentially important technologically as electron field emitters (e.g. microguns, microwave amplifiers, displays), nanoelectrodes for sensors, filter media, superhydrophobic surfaces and thermal interface materials for microelectronics. A parametric study on the growth of CN grown by glow discharge dc-PECVD is presented. In this technique, a substrate containing thin film Ni catalyst is exposed to C_2H_2 and NH_3 gases at $700^\circ C$. Without plasma, this process is essentially thermal CVD which produces curly spaghetti-like CN as seen in Fig. 1(a). With the plasma generated by biasing the substrate at $-600V$, we observed that the CN align vertically during growth as shown in Fig. 1(b), and that the magnitude of the applied substrate bias affects the degree of alignment. The thickness of the thin film Ni catalyst was found to determine the average diameter and inversely the length of the CN. The yield and density of the CN were controlled by the use of different diffusion barrier materials under the Ni catalyst. Patterned CN growth [Fig. 1(c)], with 1σ variation in CN diameter of 4.1% and 6.3% respectively, is achieved by lithographically defining the Ni thin film prior to growth. The shape of the structures could be varied from very straight nanotube-like to conical tip-like nanofibers by increasing the ratio of C_2H_2 in the gas flow. Due to the plasma decomposition of C_2H_2 , amorphous carbon (a-C) is an undesirable byproduct which could coat the substrate during CN growth. Using a combination of depth profiled Auger electron spectroscopy to study the substrate and in-situ mass spectroscopy to examine gas phase neutrals and ions, the optimal conditions for a-C free growth of CN is determined.

The role of the plasma in a dc plasma enhanced chemical vapor deposition system for carbon nanofiber growth is investigated with a 1-D radially averaged computational model [1]. Equations for the conservation of species mass, ion momentum, and ion, electron, and neutral gas thermal energy are solved axially between the anode and cathode. The model includes 28 species and 200 reactions. The plasma decomposes the ammonia and acetylene feedstock through electron impact dissociation and ionization along with the endothermic ion-molecule sheath reactions of dissociative proton abstraction and collision-induced dissociation. These plasma reactions generate radicals that further contribute to decomposing the feedstock by way of radical exchange reactions (e.g. $NH_3 + H \rightarrow NH_2 + H_2$ and $C_2H_2 + N \rightarrow CH + HCN$). The result is the conversion of the feedstock to the more stable species of H_2 , N_2 , and HCN . The dramatic impact of this plasma-sponsored conversion on carbon nanofiber growth has been previously demonstrated [2], whereby, at the same substrate temperature, higher plasma power conditions result in much shorter nanofibers relative to lower power growth conditions. This is attributed to acetylene decomposing more readily on Ni catalyst than HCN given that the C-N triple bond strength [3] is 748 kJ/mol and the H-CCH bond strength is only 556 kJ/mol. In-situ mass spectrometry was used to confirm the simulation findings/model as shown in Fig. 2, which displays the mole fraction trends with plasma power for the three main plasma products. The trends are reproduced well where hydrogen and hydrogen cyanide increase with increasing power and nitrogen remains relatively flat. Furthermore, the simulation model has been used to predict the surface temperature at the PECVD cathode for various plasma powers, and this has been experimentally verified.

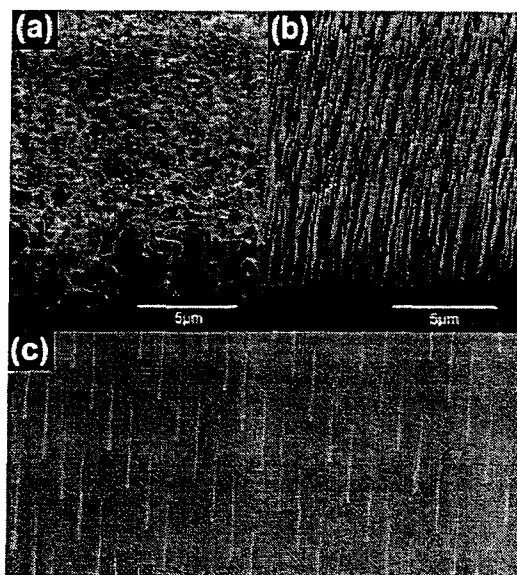


Figure 1. (a) Thermal CVD of curly CN. (b) PECVD of vertically aligned CN. (c) Patterned deposition of highly uniform CN.

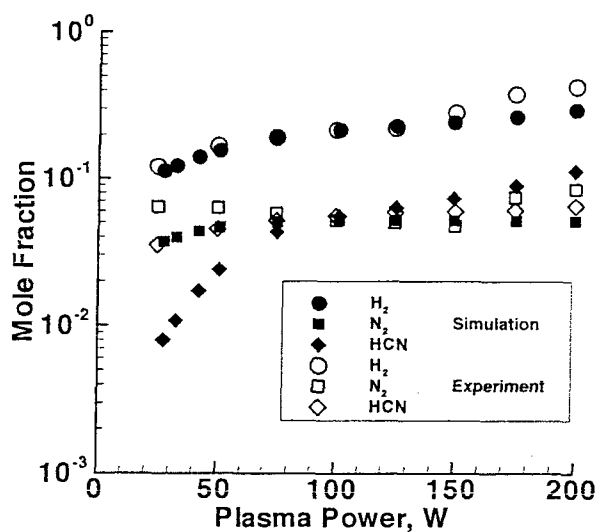


Figure 2. Mole fraction trends of main plasma products from simulation and experiment at 1 cm from cathode.

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- [3] D. R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, 81st Edition (CRC Press, Boca Raton, 2000).